First principles thermodynamics of alloys

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ABSTRACT

We present a brief report on the methods of solid state physics (electronic structure, statistical thermodynamics) that allow us to discuss the phase stability of alloys and to determine their phase diagrams.

1. INTRODUCTION

Metallic alloys display many different ordered structures either on different crystalline structures (A15 phases, σ phases, Laves phases, etc.) or on fixed, and generally simple, underlying structures. The B2 (CsCl) and $L1_2$ (Cu_3Au) ordered structures are canonical examples of such structures built on the BCC and FCC structures, respectively (Fig.1).

Figure 1. B2 (CsCl-type) and $L1_2$ (Cu_3Au -type) ordered structures.

Even in this case, the phase diagrams, with order-disorder transitions below the melting points (Pt-V, Ni-V) or not (Ti-Al), can be fairly complex. We would like to understand such phase diagrams from "first principles" methods. Ordering effects on the other hand have many important consequences concerning the physical properties of the alloys as well as their mechanical properties (γ - γ' superalloys, intermetallics,...)

The interatomic interactions on a fixed lattice may favour homoatomic or heteroatomic first neighbour pairs. This generally induces phase separation or ordering. Schematic phase diagrams corresponding to these two situations are sketched in Fig.2.

The general question is therefore: what stabilizes a given structure at fixed concentration and temperature? "Old" but still quite valuable theories were mostly based on phenomenological criteria involving size effects, electronegativity, or simple electronic structure arguments (Hume Rothery theory, Pettifor's structure maps; for a more complete discussion, see [1]). Similarly the phase diagrams are usually calculated using phenomenological macroscopic thermodynamics (Calphad approach).

In order to calculate the free energy $F = U - TS$ within the simplest microscopic theories, it is natural to consider the internal energy U and the entropy S separately. The internal energy is principally determined by electronic calculations performed at zero temperature. This can now be achieved in the case of simple ordered compounds, but approximations have to be introduced to treat partially ordered states. The

entropy on the other hand is essentially a configurational entropy which can now be calculated with a high accuracy. Additional contributions coming from lattice vibrations should also be included, but first principles methods are not really available at the present time to calculate them. More generally, the techniques we are going to describe principally apply to rigid lattices, which means that size effects are assumed to be small.

Figure 2. Typical phase diagrams for phase separation and ordering; α and α' are solid solutions; β is an ordered phase.

2. ELECTRONIC STRUCTURE

Total energies of simple intermetallic compounds can now be calculated with a very good accuracy, using the so-called local density functional approximation and appropriate techniques to determine the band structure (LMTO, LAPW, etc.). The accuracy is sufficient in particular to distinguish between several types of order. For example recent calculations have been made concerning Ni_3V , Co_3V and Fe_3V [2]; the L1_2 , DO_{22} and DO_{19} ordered structures have been compared and the correct ground states have been obtained in all cases. It should be noticed that typical energy differences are of the order of a few 10 mRyd/at. whereas the total energies are of the order of 10^4 Ryd/at.

Now, models are necessary to predict and understand trends, to deal with partially disordered states and to work at finite temperature. Let $E(\{p_n\})$ be the energy of any atomic configuration of a binary alloy, the p_n being occupation numbers, equal to unity if site n is occupied by an A atom and to zero if it is occupied by a B atom. The hope is that this energy can be written as an expansion in terms of multiautom interactions

$$E(\{p_n\}) = E_0 + \frac{1}{2} \sum_{n,m} V_{nm} p_n p_m + \frac{1}{3!} \sum_{n,m,p} V_{nmp} p_n p_m p_p + \dots$$

where for instance V_{nm} is equal to $V_{nm}^{AA} + V_{nm}^{BB} - 2V_{nm}^{AB}$, the V_{nm}^{ij} being the pair interaction between atoms of types i and j at sites n and m . In fact such a development has been shown to be convergent in many cases, provided the medium of reference is judiciously chosen [1]. In principle, good convergence requires the interactions to be dependent on the concentration. If only pair interactions are retained we have a model completely similar to the Ising model.

Several methods are used to calculate the interactions. One can postulate an expansion with a finite set of interactions and perform first principles calculations for different ordered structures, i.e. for different set of $\{p_n\}$. It is then sufficient to inverse a linear system to get the interactions. This is the so-called Conolly-Williams inversion scheme. The advantage of the method is that it uses the very reliable electronic structure calculations. On the other hand there is no real criterion to decide what types of interactions are to be kept or not. It is therefore preferable in principle to start from a theory providing explicit expressions for the interactions. This can be done using a generalized perturbation method which compares the energy of a given

configuration with that of the fully disordered state treated within the coherent potential approximation (CPA). The trends can be obtained quite easily using the tight-binding approximation and moment arguments. More quantitative results have been obtained using the tight-binding method and the CPA or the more accurate KKR-CPA method [1,3,4, and references therein].

We just mention here that this theory predicts that on the FCC lattice first neighbour interactions should be generally dominant and that third and fourth neighbour interactions should have the same order of magnitude as second neighbour ones. Multiatom interactions of higher order are smaller. Similar types of hierarchies can be predicted on any lattice. In this scheme, the pair interactions depend on the concentration. They also increase when the difference ΔN_e between the numbers of valence electrons of the alloy constituents increase. In the case of transition alloys, one also find simple trends for the ordering tendencies. Order is favoured for half-filled d bands and phase separation for almost empty or filled d bands, the filling of the band being determined by the mean number N_e of valence electrons. A typical variation of the first neighbour interaction V_1 responsible for the major part of the ordering energy is sketched in Fig.3.

Figure 3. Typical variation of the first neighbour pair interaction for transition equiconcentration alloys, as a function of the filling of the d band.

3. GROUND STATES

At zero temperature, the stablest ordered structure is that minimizing the energy. This is not an obvious problem because of frustration effects. By this we mean for example that it is not always possible to fill a lattice with heteroatomic (A-B) first neighbour pairs. This is the case when looking for ordered structures on the FCC lattice driven by first neighbour interactions. There are triangles and tetrahedra of first neighbour bonds which obviously cannot all be heteroatomic. This is a geometrical effect. Similar difficulties can arise in the presence of competing interactions. In fact the problem of minimizing the energy reduces to a linear programming problem where the constraints are deduced from a study of the possible atomic configurations of finite clusters (triangles, tetrahedra,...). In practice explicit solutions are only available when the interactions are short-ranged. A detailed account of the relevant formalism, first developed by Kanamori and his coworkers is given in Ref.[1]. As an example we present in Fig.4 the results concerning the FCC lattice with first and second neighbour interactions.

Figure 4. Ground state of the FCC lattice with first and second neighbour interactions. Descriptions of the structures can be found in Ref.[1-4].

Of particular interest is the comparison between the $L1_2$ and DO_{22} structures shown in Fig.5. Both structures have the same number of first neighbour AB pairs so that the energy difference between them is expected to be very small, of the order of a few 10^{-2}eV instead of a few 10^{-1}eV usually. This energy difference is proportional to $V_2 - 4V_3 + 4V_4$ in an analysis up to fourth neighbours. The result of a calculation for transition alloys within the tight-binding approximation [5] is shown in Fig.6. It predicts in particular a

stability exchange for band filling N_e about seven, in good agreement with the observed structures; Pd_3V ($N_e = 7.75$) is DO_{22} whereas Rh_3V ($N_e = 7$) is L1_2 . These results have been confirmed by more sophisticated electronic structure calculations which give a critical value for N_e about 7.6 [2,6].

Figure 5. L1_2 and DO_{22} ordered structures.

A further experimental evidence for this L1_2 - DO_{22} competition has been recently obtained through a study of pseudobinary alloys $(\text{Pt-Rh})_3\text{V}$ and $(\text{Pd}_3\text{Rh})_3\text{V}$ alloys [7].

Figure 6. Calculated energy difference between L1_2 and DO_{22} as a function of the number of d electrons. Continuous line: full calculation; dotted line: calculation with pair interactions up to V_4 [5].

There are numerous other examples showing that simple theoretical arguments predict the correct structural trends. For example the hierarchy between the interactions on a FCC lattice shows that it is generally necessary to include third and fourth neighbour interactions as soon as second neighbour interactions are introduced. This is frequently verified, in the case of transition alloys at least. Actually many observed ordered structures require at least fourth neighbour interactions to be stabilized. Conversely a structure like that of CuPt (L1_1) requires second neighbour interactions comparable with the first neighbour ones and is in fact never observed except precisely in the case of CuPt !

As another example illustrating how we have elucidated trends, consider the nickel-based transition alloys, in particular their phase diagrams as compiled by De Boer et al.[8]. When ΔN_e is small, ordering is absent except in Pt-Ni . Small values of ΔN_e imply small, almost unobservable transition temperatures, and anyway large values of N_e induce a tendency to phase separation. For the case of 4d and 5d alloying elements, except for Pt-Ni , there is indeed no ordering tendency up to Tc and Re . Ordering effects in Ni-Fe and Ni-Mn are clearly correlated with the appearance of magnetism. Weak ordering effects appear when ΔN_e increases. Ni-Mo and Ni-W present ordered phases whereas SRO effects have clearly been detected in Ni-Cr . This is consistent with the fact that the order of magnitude of ordering energies should increase with the bandwidth, i.e. when going from the 3d to the 5d series. The same phenomenon exists for the vanadium column: on the Ni-rich side of the diagrams there are ordered structures on the FCC lattice which disorder at high temperature in the case of Ni-V but not in the case of Ni-Nb and Ni-Ta . Finally many very stable ordered compounds appear when ΔN_e is equal to 6 and 7. Thus, except for the ordering in Pt-Ni which is still a subject of controversy, almost all is understood qualitatively for the case of Ni-based alloys. This is certainly a somewhat favourable situation, but many other successful analyses have been made. For example, the fact that off-diagonal disorder induces phase separation is well verified in the case of Cr-Mo and Cr-W alloys.

4. THERMODYNAMICS

At finite temperature we must handle thermodynamic averages. The average of a quantity O depending on the configurations C of the alloy is given by

$$\langle O \rangle = \sum_C \rho(C) O(C) \quad ; \quad \rho(C) = \exp[-E(C)/k_B T] / Z$$

where Z is the partition function. The correlation functions in particular are just the averages of products of occupation numbers p_n . In a solid solution the one-point correlation function $\langle p_n \rangle$ is obviously equal to the concentration. In an ordered state, translational symmetry is broken and these averages depend on the sublattice containing site n . For example in the case of the B2 ordered structure, we have two simple cubic sublattices whose concentration are equal to $(1 \pm \phi)/2$ where ϕ is by definition the long range order parameter. Pair correlation functions $\langle p_n p_m \rangle$ on the other hand are related to the familiar Warren Cowley short-range order parameters $\alpha(m-n)$

$$\langle p_n (1 - p_m) \rangle = c(1-c)[1 - \alpha(m-n)]$$

The Ising model is generally not solvable exactly and the simplest form for the free energy is obtained using the mean field Bragg-Williams-Gorsky approximation

$$F = \frac{1}{2} \sum_{n,m} V_{nm} c_n c_m + k_B T \sum_n [c_n \log c_n + (1-c_n) \log(1-c_n)]$$

Varying these equations yield self-consistent equations for the c_n i.e. for the long-range order parameters. This approximation is fairly good qualitatively but not quantitatively. The order-disorder transition temperatures in particular are too high. In the presence of frustration effects, the qualitative shape of the phase diagrams may even be wrong. Almost exact calculations can now be performed using either Monte Carlo simulations or improved mean field theories such as the cluster variation method (CVM) of Kikuchi. A comparison between the results obtained using the simple mean field theory [9] and the tetrahedron-octahedron CVM is shown in Fig. 7. A more accurate discussion can be found in Ref.[10-12].

Figure 7. Schematic phase diagram of the FCC lattice with first neighbour interactions V calculated within the mean field approximation (left) and within the tetrahedron-octahedron CVM approximation (right).

The short-range order parameters can be measured from diffuse X-ray or neutron scattering experiments. Using then inverse CVM or Monte Carlo techniques the pair interactions can be determined and compared with the values obtained from electronic structure calculations. This is becoming a very accurate and fruitful tool (for a recent review, see Ref.[13]).

It is more difficult to calculate realistic phase diagrams than to characterize the single phases, one reason being that it is not sufficient to know the interatomic interactions. The free energy of the disordered state is also required. Although it can be calculated in principle, using the CPA for example, additional contributions related to elastic, vibrational and other effects have to be included. Another serious difficulty is that real phase diagrams frequently involve different crystalline structures, and at the moment there is no elaborate theory to describe the interplay between structural and chemical (ordering) effects. In practice, ordering effects are treated on fixed lattices and the free energies for different structures are compared.

This is a correct procedure but the uncertainties concerning the structural energies or entropies are difficult to estimate, and generally some parameters have to be fitted to experimental data in order to produce reasonable phase diagrams. It is clear also that it is difficult to treat the liquid state on the same footing than the solid phases.

Despite all these problems several phase diagrams have now been calculated. There is no room here to undertake a comprehensive review of these results. We just mention some calculations concerning the Ti-Rh [14] Ni-Cr [15] Pd-Rh, Al-Li [16] phase diagrams and the recent detailed discussions concerning the Ni-Ti, Ni-Al, Ti-Al and Cd-Mg phase diagrams [17,18, 19, 20]. The experimental and calculated diagrams of Ti-Ni are shown in Fig.8.

Figure 8. Experimental and calculated phase diagram of Ti-Ni [17].

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